

# Effect of pH/Auxiliary Ligand on the Structures of Coordination Compounds Based on a Novel Ligand 2,6-Bis(pyrazin-2-yl)pyridine-4-carboxylate

SONG Juan<sup>1</sup>(宋娟);HU Huai-Ming<sup>2</sup>(胡怀明);SHI Juan<sup>1</sup>(史娟);JI Jian-Wei<sup>1</sup>(季建伟);LU Jiu-Fu<sup>1</sup>(卢久富);GE Hong-Guang<sup>1</sup>(葛红光)

<sup>(1)</sup> Shaanxi Key Laboratory of Catalysis, College of Chemical & Environment Science, Shaanxi University of Technology, Hanzhong 723001, China; <sup>(2)</sup> Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, China

**ABSTRACT** Four new coordination compounds,  $[\text{Zn}(\text{bppc})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  (**1**),  $[\text{Zn}_2(\text{bppc})_2(\text{m-bdc})(\text{H}_2\text{O})_4] \cdot 7\text{H}_2\text{O}$  (**2**),  $[\text{Zn}(\text{bppc})_2(\text{H}_2\text{O})_2]_n \cdot n(\text{m-Hbdc}) \cdot n(\text{H}_2\text{O})$  (**3**),  $[\text{Zn}_2(\text{bppc})(\text{btc})(\text{H}_2\text{O})_3]_n \cdot 5n\text{H}_2\text{O}$  (**4**) (Hbppc = 2,6-bis(pyrazin-2-yl)pyridine-4-carboxylate,  $\text{H}_2(\text{m-bdc})$  = 1,3-benzenedicarboxylic acid,  $\text{H}_3\text{btc}$  = 1,3,5-benzene-tricarboxylic acid), have been hydrothermally synthesized and structurally characterized. Compound **1** shows a mononuclear structure and **2** shows a dinuclear structure. Compound **3** is a one-dimensional chain structure, which is extended into a 3D supramolecular network by intermolecular hydrogen interactions. In **4**, a 1D loop-like chain is connected by  $(\text{btc})^{3-}$  anions to generate a 2D layer structure. The structure differences of **1**~**4** show that the pH and aromatic acid as auxiliary ligand have important influence on the final structures. Additionally, the luminescent properties of **1**~**4** have been investigated with fluorescent spectra in the solid state, and **1**~**4** display a strong fluorescent emission at room temperature and have potential applications as fluorescent-emitting materials.

**Keywords:** crystal structure; hydrothermal synthesis; coordination polymer, luminescence;

**DOI:** 10.14102/j.cnki.0254-5861.2011-1633

## 1 INTRODUCTION

Received 9 March 2017; accepted 29 June 2017 (CCDC 966809 for **1**, 966810 for **2**, 966811 for **3** and 966812 for **4**)

① Supported by the Introducing Talents Foundation of Shaanxi Sci-Tech University (No. SLGKYQD2-08) and National Natural Science Foundation of China (No. 21502109)

② Corresponding author. Song Juan (1983-), instructor, doctor, majoring in coordination chemistry. E-mail: sj-528@163.com

In the last couple of decades, more and more researchers have been paid considerable attention to the construction of various coordination compounds not only due to their multiple applications as functional materials in many fields such as luminescence, chemical and biological sensor, separation, magnetism, catalysis, gas adsorption, ion exchange, chirality, *etc*<sup>[1-9]</sup>, but also for their intriguing architectures and fascinating topologies<sup>[10]</sup>. Among them, zero-dimensional (0D) multinuclear complexes, one-dimensional (1D) helical and zigzag chains, two-dimensional (2D) grids, three-dimensional (3D) porous structures, and interpenetrating networks have been presented<sup>[11]</sup>. Although a variety of metal coordination frameworks with beautiful topologies and interesting properties have been synthesized, it is a great challenge to control structures with desired properties, because many factors affect the result, such as the selection of solvent system, reaction temperature, time, pH, organic ligand, metal ion, the ratio between metal and ligand, counterion and so on<sup>[12-15]</sup>. The effective and facile approach to overcome this problem is the appropriate choice of well-designed organic bridging ligands containing modifiable backbones and connectivity information, together with the metal centers with various coordination preferences.

Our group is interested in the ternary compounds constructed from the rigid N-donor ligands (polypyridine or pyrazine), O-donor ligands (polycarboxylate) and  $d^{10}$  transitional metal ions. 2,6-Bis(pyrazin-2-yl)pyridine-4-carboxylic acid (Hbppc, Chart 1), as a rigid planar ligand, has not been reported in the realm of chemistry. It possesses several interesting structure characterizations. Firstly, it contains five nitrogen and two oxygen atoms from one pyridyl, two pyrazinyl and one carboxyl groups, thus it can function as either chelating or bridging ligand. Secondly, the carboxyl and N-heterocyclic groups can act not only as hydrogen-bond acceptors but also as hydrogen-bond donors, depending upon the deprotonation and protonation, which is beneficial for the construction of supramolecular architectures. In addition, the extended conjugated system can easily form  $\pi$ - $\pi$  interactions which have greatly influence the constructing supramolecular framework. Therefore, Hbppc as a good candidate has attracted our interest for the construction of metal-organic supramolecular architectures.

In addition to coordination bonding, other noncovalent interactions, such as hydrogen bonds<sup>[16]</sup> and  $\pi$ ... $\pi$  interactions<sup>[17]</sup>, also greatly affect the structures of coordination polymers, and they may link multinuclear discrete subunits or low-dimensional entities into high-dimensional supramolecular networks to make the whole structure stable. In this work, by using Hbppc ligand and changing the pH and/or using auxiliary ligands, a series of coordination polymers  $[\text{Zn}(\text{bppc})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  (**1**),  $[\text{Zn}_2(\text{bppc})_2(\text{m-bdc})(\text{H}_2\text{O})_4] \cdot 7\text{H}_2\text{O}$  (**2**),

$[\text{Zn}(\text{bppc})(\text{H}_2\text{O})_2]_n \cdot n(\text{m-Hbdc}) \cdot n(\text{H}_2\text{O})$  (**3**) and  $[\text{Zn}_2(\text{bppc})(\text{btc})(\text{H}_2\text{O})_3]_n \cdot 5n\text{H}_2\text{O}$  (**4**), were prepared under hydrothermal conditions. Moreover, their luminescent property and thermal stability were also investigated.

## 2 EXPERIMENTAL

### 2.1 Materials and general method

Hbppc ligand was prepared according to literature method with some modifications<sup>[18]</sup>. Other chemicals and reagents were purchased commercially and used without further purification. Elemental analyses (C, H, N) were determined with a Vario EL III elemental analyzer. Infrared spectra were recorded on a Bruker EQUINOX55 spectrometer as KBr pellets in the range of  $4000 \sim 400 \text{ cm}^{-1}$ . Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Thermal gravimetry analyses (TGA) were carried out with a Universal V2.6 DTA system at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  in a nitrogen atmosphere.

### 2.2 Synthesis of Hbppc

A mixture of 2-furaldehyde (1.92 g, 2 mmol), acetylpyrazine (4.88 g, 4 mmol) and crushed NaOH powder (1.60 g, 40.0 mmol) was dissolved in ethanol (100 mL) and stirred at  $60 \text{ }^\circ\text{C}$  for 24 h, resulting in the formation of a red solution. And then, after the mixture was cooled to room temperature, the mixture was filtered off, and dried in a vacuum to give 2.0 g 4-furan-2-yl-2,6-diphenyl-pyridine. After that,  $\text{KMnO}_4$  (3.21 g, 26.7 mmol) and water (100 mL) were added, the pH was adjusted to 9 with NaOH, and stirred at  $80 \text{ }^\circ\text{C}$  for 1 h. After the mixture was cooled to room temperature, the resulting mixture was filtered off, followed by adjusting the pH to 5 with HCl. Then the resulting mauve precipitate was filtered off, recrystallized with methanol, and dried in a vacuum to give 2.41 g (yield 32.4%) Hbppc as colourless needle crystals. Anal. Calcd. (%) for  $\text{C}_{14}\text{H}_9\text{N}_5\text{O}_2$ : C, 168.15; H, 9.07; N, 70.04; O, 32.00. Found (%): C, 168.09; H, 8.98; N, 70.01; O, 31.89. IR (KBr,  $\text{cm}^{-1}$ ): 3414(s), 2474(w), 1898(w), 1617(s), 1524(w), 1467(w), 1370(m), 1252(m), 1164(w), 1108(m), 1081(w), 856(m), 776(m), 750(w), 679(w), 617(w), 484(w).

### 2.3 Synthesis of $[\text{Zn}(\text{bppc})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**1**)

A mixture of Hbppc (27.9 mg, 0.1 mmol) and  $\text{ZnCl}_2$  (27.3 mg, 0.2 mmol) in deionized water (10 mL) was stirred while adjusting the pH to 5.5 with 0.2 mol/L NaOH. After being stirred for 30 min, the mixture was sealed in a 25 mL Teflon-lined stainless-steel vessel and heated to  $160 \text{ }^\circ\text{C}$  for 96 h. Then the reaction system was cooled to room temperature during 48 h to give rise to colorless block crystals of **1** in ca. 50% yield based

on Zn, which were collected by filtration and washed with deionized water. Anal. Calcd. for  $C_{28}H_{16}N_{10}O_9Zn$  (701.88): C, 47.91; H, 2.3; N, 19.96%. Found: C, 47.93; H, 2.5; N, 19.95%. IR(KBr,  $cm^{-1}$ ): 3385(s), 1621(s), 1560(m), 1468(w), 1431(w), 1377(s), 1321(s), 1233(w), 1166(m), 1136(w), 1108(w), 1034(m), 916(w), 857(w), 824(w), 791(w), 767(w), 699(w), 621(w), 495(w).

#### 2.4 Synthesis of $[Zn_2(bppc)_2(m-bdc)(H_2O)_4] \cdot 7H_2O$ (2)

A mixture of Hbppc (27.9 mg, 0.1 mmol),  $ZnCl_2$  (27.3 mg, 0.2 mmol) and  $H_2(m-bdc)$  (16.6 mg, 0.1 mmol) in deionized water (10 mL) was stirred and the pH was then adjusted to 5.5 with 0.2 mol/L NaOH. After being stirred for 30 min, the reaction mixture was sealed in a Teflon-lined stainless-steel vessel and heated to 160 °C for 96 h. Then the reaction system was cooled to room temperature during 48 h to give rise to colorless sheet crystals of **2** in ca. 50% yield based on Zn, which were collected by filtration and washed with deionized water. Anal. Calcd. for  $C_{36}H_{42}N_{10}O_{19}Zn_2$  (1049.55): C, 41.20; H, 4.03; N, 13.35%. Found: C, 41.21; H, 4.025; N, 13.31%. IR (KBr,  $cm^{-1}$ ): 3415(m), 1615(s), 1562(m), 1456(m), 1403(m), 1375(vs), 1331(m), 1168(m), 1089(w), 1038(m), 861(w), 792(w), 745(w), 711(w), 683(w), 463(w).

#### 2.5 Synthesis of $[Zn(bppc)_2(H_2O)_2]_n \cdot n(m-Hbdc) \cdot n(H_2O)$ (3)

Compound **3** was synthesized similar to that of **2**, except changing the pH to 6.5. Yellow block crystals were obtained in ca. 50% yield based on Zn. Anal. Calcd. for  $C_{22}H_{19}N_5O_9Zn$  (562.79): C, 46.95; H, 3.4; N, 12.44%. Found: C, 46.94; H, 3.5; N, 12.43%. IR(KBr,  $cm^{-1}$ ): 3421(m), 1609(s), 1458(w), 1375(s), 1170(m), 1036(m), 916(w), 860(w), 793(w), 743(m), 714(m), 683(w), 528(w), 462(w).

#### 2.6 Synthesis of $[Zn_2(bppc)(btc)(H_2O)_3]_n \cdot 5nH_2O$ (4)

Compound **4** was synthesized similar to that of **2**, except using  $H_3btc$  instead of  $H_2(m-bdc)$ . Colourless block crystals were obtained in ca. 65% yield based on Zn. Anal. Calcd. for  $C_{23}H_{27}N_5O_{16}Zn_2$  (760.26): C, 36.34; H, 3.58; N, 9.21%. Found: C, 36.32; H, 3.56; N, 9.19%. IR(KBr,  $cm^{-1}$ ): 3416(m), 2026(w), 1618(s), 1562(m), 1426(m), 1376(s), 1183(m), 1066(w), 1035(m), 913(w), 766(w), 714(m), 687(w), 612(w), 548(w), 460(w), 414(w).

#### 2.7 X-ray crystallography

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares based on  $F^2$  using SHELXTL-97 program<sup>[19]</sup>. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Selected bond distances and bond angles for

**1**~**4** are listed in Table **1**~**4**.

### 3 RESULTS AND DISCUSSION

#### 3.1 Structure description of **1**

Single-crystal X-ray analysis reveals that **1** crystallizes in triclinic system, space group  $P\bar{1}$ , with  $a = 7.165(6)$ ,  $b = 11.482(10)$ ,  $c = 19.018(17)$  Å,  $\alpha = 88.973(16)^\circ$ ,  $\beta = 85.533(16)^\circ$ ,  $\gamma = 72.386(17)^\circ$ ;  $Z = 1$  and is a mononuclear structure, as shown in Fig. 1a. The asymmetric unit of **1** consists of one  $\text{Zn}^{\text{II}}$  cation, two  $(\text{bppc})^-$  anions, two coordination water and three lattice water molecules. Zn(1) is hexa-coordinated by three nitrogen atoms[N(1), N(3), N(4)] and one oxygen atom O(3) from  $(\text{bppc})^-$  anions and two oxygen atoms[O(5), O(6)]from coordination water molecules with a distorted octahedral geometry. The N(1), N(3), N(4), and O(3) atoms comprise the equatorial plane and the O(5) and O(6) atoms occupy the axial positions. The Zn–N and Zn–O bond lengths fall in the ranges of 2.059(8)~2.203(10) and 1.928(7)~2.234(7) Å, respectively, which are consistent with the corresponding values reported for Zn-pyridyl and Zn-carboxylate complexes<sup>[20]</sup>. In **1**, two  $(\text{bppc})^-$  anions coordinate to a  $\text{Zn}^{\text{II}}$  cation with monodentate (Scheme 1a) and tridentate chelating (Scheme 1b) coordination modes to form a mononuclear structure. The adjacent mononuclear units are interconnected via intermolecular hydrogen bonding interactions between the nitrogen atoms of  $(\text{bppc})^-$  ligands and oxygen atoms of coordination water molecules ( $\text{N}(2) \cdots \text{O}(5)$ , 2.828 Å), oxygen atoms of coordination water molecules and the oxygen atoms of  $(\text{bppc})^-$  ligands ( $\text{O}(6) \cdots \text{O}(1)$ , 2.737 Å) to form a 1D chain (Fig. 1b). Furthermore, these adjacent chains are further connected via hydrogen bonding interactions between N atoms of  $(\text{bppc})^-$  ligands and O atoms of lattice water molecules ( $\text{N}(10) \cdots \text{O}(7) = 2.721$  Å), O atoms of coordinated water molecules and O atoms of lattice water molecules ( $\text{O}(7) \cdots \text{O}(6) = 2.582$  Å) to form a 2D supramolecular structure (Fig. 1c).

#### 3.2 Structure description of **2**

Single-crystal X-ray analysis reveals that **2** crystallizes in triclinic system, space group  $P\bar{1}$ , with  $a = 9.9357(11)$ ,  $b = 10.5755(12)$ ,  $c = 21.343(2)$  Å,  $\alpha = 80.253(2)^\circ$ ,  $\beta = 79.653(2)^\circ$ ,  $\gamma = 76.851(2)^\circ$  and  $Z = 2$ . Compound **2** displays a dinuclear structure, as shown in Fig. 2a. The asymmetric unit of **2** contains two crystallographically independent  $\text{Zn}^{\text{II}}$  cations, two  $(\text{bppc})^-$  and one  $(\text{m-bdc})^{2-}$  anions, four coordination water and seven lattice water molecules. Zn1 is coordinated by three nitrogen atoms from one  $(\text{bppc})^-$  anion ( $\text{Zn}(1)\text{--N}(1) = 2.284(3)$  Å,  $\text{Zn}(1)\text{--N}(3) = 2.126(3)$  Å,  $\text{Zn}(1)\text{--N}(4) = 2.176(3)$  Å) and three oxygen atoms from

(m-bdc)<sup>2-</sup> anion and two coordination water molecules (Zn(1)–O(5) = 1.969(3), Zn(1)–O(9) = 2.158(3), Zn(1)–O(10) = 2.110(3), Zn(1)–O(10) = 2.186(3) Å), showing a distorted octahedral coordination geometry. The Zn2 has similar coordination geometry with Zn1. In **2**, one (bppc)<sup>-</sup> anion coordinates to the Zn<sup>II</sup> cation with a chelating coordination mode (Scheme 1b) to form a mononuclear unit, and such two units are bridged by (m-bdc)<sup>2-</sup> anion with a  $\mu_2$ - $\eta^1$ : $\eta^1$  coordination mode to form a dinuclear [Zn<sub>2</sub>(bppc)<sub>2</sub>(m-bdc)(H<sub>2</sub>O)<sub>4</sub>] structure. The adjacent dinuclear units are interconnected via intermolecular hydrogen-bonding interactions between O atoms of (m-bdc)<sup>2-</sup> anion, N atoms of (bppc)<sup>-</sup> ligands and oxygen atoms of coordination water molecules (N(2)··O(10), 2.678 Å), O atoms of coordination water molecules and O atoms of (bppc)<sup>-</sup> ligands (O(12)··O(4), 2.844 Å) to form a one-dimensional chain (Fig. 2b). The adjacent chains are further extended into a 2D supramolecular layer (Fig. 2c).

### 3.3 Structural description of 3

Single-crystal X-ray analysis reveals that **3** crystallizes in orthorhombic system, space group *Pna*2<sub>1</sub>, with *a* = 17.7527(15), *b* = 17.5479(15), *c* = 7.3095(6) Å, and *Z* = 4. **3** is a one-dimensional chain structure, as shown in Fig. 3a. The asymmetric unit of **3** consists of one Zn<sup>II</sup> cation, one (bppc)<sup>-</sup> ligand, one (m-Hbdc)<sup>-</sup> counter anion, two coordination water and one lattice water molecules. The Zn(1) is hexa-coordinated by three nitrogen atoms (N(1), N(3), N(4)) and one oxygen atom O(2) from one (bppc)<sup>-</sup> anion and two oxygen atoms (O(7), O(8)) from two coordination water molecules with a distorted octahedral geometry. The N(1), N(3), N(4) and O(2) atoms comprise the equatorial plane and the O(7) and O(8) atoms occupy the axial positions. Each (bppc)<sup>-</sup> anion coordinates to one Zn<sup>II</sup> atom with its chelating nitrogen atoms and the Zn<sup>II</sup> atoms are further bridged by the carboxylate oxygen atoms of another (bppc)<sup>-</sup> anion (Chart 2c) to form a one line-like dimensional chain (Fig. 3b).

The line-like chains are further extended into a 2D supramolecular structure through intermolecular hydrogen bonding interactions between O atoms of coordination and lattice water molecules (O(7) ··· O(9) = 2.721 Å), as well as between O atoms of lattice water molecules and (m-Hbdc)<sup>-</sup> counter anion (O(9) ··· O(5) = 2.921 Å, O(9) ··· O(3) = 2.759 Å) (Fig. 3c). The 2D supramolecular structure is finally extended into a 3D supramolecular structure through intermolecular hydrogen-bonding interactions of coordination water molecules, (m-Hbdc)<sup>-</sup> counter anion and (bppc)<sup>-</sup> anion (Fig. 3d).

### 3.4 Structural description of 4

The single-crystal X-ray diffraction analysis reveals that **4** crystallizes in monoclinic system, space group *P*2<sub>1</sub>/*c* with *a* = 14.726(2), *b* = 14.613(2), *c* = 13.7709(19) Å,  $\beta$  = 111.2552(2)° and *Z* = 4. **4** displays a

two-dimensional supramolecular structure composed of one-dimensional chains. The asymmetric unit of **4** contains two crystallographically independent  $\text{Zn}^{\text{II}}$  cations, one  $(\text{bppc})^-$  and one  $(\text{btc})^{3-}$  anions, three coordination water and five lattice water molecules. As shown in Fig. 4a, the  $\text{Zn}(1)$  atom is coordinated by three nitrogen atoms from one  $(\text{bppc})^-$  anion ligand ( $\text{Zn}(1)-\text{N}(1) = 2.210(4) \text{ \AA}$ ,  $\text{Zn}(1)-\text{N}(3) = 2.135(4) \text{ \AA}$ ,  $\text{Zn}(1)-\text{N}(4) = 2.242(4) \text{ \AA}$ ), one carboxylic oxygen atom of  $(\text{btc})^{3-}$  anion ( $\text{Zn}(1)-\text{O}(6) = 1.993(4) \text{ \AA}$ ) and two oxygen atoms of two different coordination water molecules ( $\text{Zn}(1)-\text{O}(9) = 2.098(4) \text{ \AA}$ ,  $\text{Zn}(1)-\text{O}(10) = 2.113(4) \text{ \AA}$ ), showing a distorted octahedral coordination geometry. The  $\text{Zn}(2)$  atom is coordinated by one nitrogen atom and one oxygen atom from one  $(\text{bppc})^-$  anion ligand ( $\text{Zn}(2)-\text{N}(5) = 2.122(4) \text{ \AA}$ ,  $\text{Zn}(2)-\text{O}(1\text{A}) = 2.070(4) \text{ \AA}$ ), three carboxylic oxygen atoms of  $(\text{btc})^{3-}$  anion ( $\text{Zn}(2)-\text{O}(3\text{C}) = 1.945(4) \text{ \AA}$ ,  $\text{Zn}(2)-\text{O}(7\text{A}) = 2.358(5) \text{ \AA}$ ,  $\text{Zn}(2)-\text{O}(8\text{A}) = 2.089(5) \text{ \AA}$ ) and one oxygen atom of coordination water molecule ( $\text{Zn}(2)-\text{O}(11) = 2.285(6) \text{ \AA}$ ) also showing a distorted octahedral coordination geometry.

Each  $(\text{bppc})^-$  anion ligand adopting a  $\mu_3-\eta^1:\eta^3:\eta^1$  mode (chart 2d) links  $\text{Zn}(1)$  and  $\text{Zn}(2)$ , each  $\text{Zn}(1)$  atom is further bridged by one  $(\text{btc})^{3-}$  anion in a  $\mu_3-\eta^1:\eta^2:\eta^1$  coordination mode and forms a 1D chain (Fig. 4b), and the  $(\text{btc})^{3-}$  anions further extend the 1D chain into a 2D supramolecular layer structure (Fig. 4c). To reduce multidimensional structures to simple node and connection nets, the  $\text{Zn}(1)$  and  $\text{Zn}(2)$  can be simply considered as a 2- and a 4-connected nodes, respectively. The  $(\text{bppc})^-$  ligand and  $(\text{btc})^{3-}$  anions can also be regarded as 3-connected linkers. By analysis, compound **3** has a  $\{4.6.8\}\{4.6^2.8^2.10\}\{6^2.8\}\{6\}$  topology (Fig. 4d).

### 3.5 Effect of the pH value and auxiliary ligand on the structures of **1**~**4**

Compounds **1**~**4** were prepared as single-phase crystalline products by hydrothermal reactions of Hbppc ligand and  $\text{ZnCl}_2$  together with or without corresponding O-donor assistant ligands. The experiments and structural research remind us to study the effects of reaction conditions on the final structures. Compounds **1** and **2** were synthesized under the same reaction conditions, except for the O-donor assistant ligands of the reactions. The  $\text{H}_2(\text{m-bdc})$  as a second ligand of **2** is completely deprotonated to coordinate with  $\text{Zn}^{\text{II}}$  which makes the structure of **2** different from that of **1**. Complexes **2** and **3** were synthesized under the same reaction conditions, except for the pH values of the reactions (pH = 5.5 for **2** and 6.5 for **3**). It was found that the influence of pH value on the structures is in fact based on the protonated extend of Hbppc ligand. For compound **2**, when pH = 5.5, the Hbppc ligand is not protonated and the  $(\text{m-bdc})^{2-}$  coordinates with  $\text{Zn}^{\text{II}}$  as an O-donor assistant ligand; but for compound **3**, when pH = 6.5 the Hbppc ligand is deprotonated to coordinate with  $\text{Zn}^{\text{II}}$  and fulfill the coordination sites of  $\text{Zn}^{\text{II}}$ . The  $[\text{H}(\text{m-bdc})]^-$  exists as a guest molecule to balance the charge and stabilize the skeleton of the compound. Compounds **3** and **4** were also isolated under the same

reaction conditions except using different auxiliary ligands ( $\text{H}_2(\text{m-bdc})$  for **3** and  $\text{H}_3\text{btc}$  for **4**), resulting in **3** possessing a 1D ladder-chain structure and **4** showing a 2D layer structure.

### 3.6 Luminescent properties

Organic-inorganic coordination polymers, especially those with  $d^{10}$  metal centers, have been investigated for their fluorescent properties and potential applications as fluorescent-emitting materials, such as light-emitting diodes (LEDs)<sup>[21]</sup>. Therefore, the photoluminescence properties of **1~4** and free ligand (Hbppc) were studied in the solid state (Fig. 5). Intense emission bands are observed at 420 and 466 nm ( $\lambda_{\text{ex}} = 290$  nm) for Hbppc, which can be assigned to the ligand-centered charge transitions, that is, the  $\pi^* \rightarrow n$  and  $\pi^* \rightarrow \pi$  transitions<sup>[22]</sup>. The bimodal emissions are also observed at 500 nm for **1**, 477 nm for **2**, 471 nm for **3** and 526 nm for **4** respectively upon excitation at 280 nm. As previously reported<sup>[23, 24]</sup>, the solid aromatic carboxylate ligands 1,3- $\text{H}_2\text{bdc}$  and  $\text{H}_3\text{btc}$  are nearly nonfluorescent in the range of 400~600 nm at ambient temperature. Compared with the free Hbppc, the main peaks in **1~4** are red-shifted, which may result from ligand-to-metal charge transfer (LMCT)<sup>[25]</sup>. Notably, a lower energy emission was also detected at 388 nm for **1**, 395 nm for **2** and 390 nm for **3** which can be attributed to the intraligand  $\pi^* \rightarrow \pi$  transition.

### 3.6 Thermogravimetric analysis

In order to characterize the thermal stability of compounds **1~4**, their thermal decomposition behavior was investigated at 30~1000 °C under nitrogen atmospheres using thermal gravimetric analysis (TGA) technique. Compound **1** first loses its lattice water molecule below 104 °C, and the weight loss found of 7.1% is consistent with that calculated (7.7%). The second stage weight loss can be detected from 108 to 150 °C attributed to the departure of coordinated water molecules (Calcd. 5.1%; Found: 4.9%). Above 348 °C, the compound begins to lose their ligands and then starts to decompose (Fig. 6a). For **2**, the weight loss of 18.28% under 116 °C corresponds to the removal of lattice and coordinated water molecules (calcd. 18.62%). Then, the weight loss of 14.84% between 160 °C to 325 °C indicates the loss of  $\text{H}_2(\text{m-bdc})$  (calcd. 15.04%), and the framework begins to collapse (Fig. 6b). Below 345 °C, compound **3** begins to lose water molecules and free  $\text{H}_2(\text{m-bdc})$  molecules. Then the decomposition of residual components starts above 360 °C (Fig. 5c). And the framework of compound **4** remains intact until heated to 338 °C and then begins to collapse (Fig. 6d). TGA results of these four coordination frameworks indicate they possess great thermal stability.

## 4 CONCLUSION



In summary, four new compounds have been synthesized by the assembly of Hbppc, different auxiliary ligands and zinc salts under hydrothermal conditions. Compounds **1~4** show intriguing 0D, 1D and 2D structures. Their structural diversities show that the pH value of the reaction system and auxiliary ligand play a significant role in the structural self-assembly process. Additionally, the hydrogen bonding interactions contributed to the formation of supramolecular architectures. Moreover, compounds **1~4** exhibit intense emissions, indicating they may be good candidates as luminescent materials.

## REFERENCES

- (1) Parent, A. R.; Crabtree, R. H.; Brudvig, G. W. Comparison of primary oxidants for water-oxidation catalysis. *Chem. Soc. Rev.* **2013**, 42, 2247–52.
- (2) Ma, S.; Yuan, D.; Wang, X.; Zhou, H. C. Microporous lanthanide metal-organic frameworks containing coordinatively linked interpenetration: syntheses, gas adsorption studies, thermal stability analysis, and photoluminescence investigation. *Inorg. Chem.* **2009**, 48, 2072–2077.
- (3) Zheng, N. F.; Bu, X. H.; Feng, P. Y. Self-assembly of novel dye molecules and  $\text{Cd}_8(\text{SPh})_{12}^{4+}$  cubic clusters into three-dimensional photoluminescent superlattice. *J. Am. Chem. Soc.* **2002**, 124, 9688–9689.
- (4) Huo, J.; Xu, T.; Liu, Y.; Daemen, L. L.; Brown, C.; Timofeeva, T. V.; Ma, S.; Zhou, H. C. Hydrogen adsorption in a highly stable porous rare-earth metal-organic framework: sorption properties and neutron diffraction studies. *J. Am. Chem. Soc.* **2008**, 130, 9626–9627.
- (5) Liu, J. W.; Chen, L. F.; Cui, H.; Zhang, J. Y.; Zhang, L.; Su, C. Y. Applications of metal-organic frameworks in heterogeneous supramolecular catalysis. *Chem. Soc. Rev.* **2014**, 43, 6011–6061.
- (6) Hui, Y. Y.; Shu, H. M.; Hu, H. M.; Song, J.; Yao, H. L.; Yang, X. L.; Wu, Q. R.; Yang, M. L.; Xue, G. L. Syntheses, structures and magnetic properties of tetranuclear and trinuclear nickel(II) complexes with  $\beta$ -diketone-functionalized pyridinecarboxylate ligand. *Inorg. Chim. Acta* **2010**, 3238–3243.
- (7) Chen, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E. B. A luminescent microporous metal-organic framework for the recognition and sensing of anions. *J. Am. Chem. Soc.* **2008**, 130, 6718–6719.
- (8) Heine, J.; Günter, J. S.; Dehnen, S. Formation of a strandlike polycatenane of icosahedral cages for reversible one-dimensional encapsulation of guests. *J. Am. Chem. Soc.* **2011**, 133, 10018–10021.
- (9) White, K. A.; Chengelis, D. A.; Zeller, M.; Geib, S. J.; Szakos, J.; Petoud, S.; Rosi, N. L. Near-infrared emitting ytterbium metal-organic frameworks with tunable excitation properties. *Chem. Commun.* **2009**, 4506–4508.
- (10) Lu, J. F.; Shi, J.; Zheng, N.; Guo, X. H. Synthesis, crystal structure, and luminescent property of a Ag(I) coordination polymer with a 3D sandwich-like framework. *Chin. J. Struct. Chem.* **2016**, 35, 319–325.
- (11) Long, J. R.; Yaghi, O. M. 2009 metal-organic frameworks issue. *Chem. Soc. Rev.* **2009**, 38, 1213–1504.
- (12) Yuan, F.; Xie, J.; Hu, H. M.; Yuan, C. M.; Xu, B.; Yang, M. L.; Dong, F. X.; Xue, G. L. Effect of pH/metal ion on the structure of metal-organic frameworks based on novel bifunctionalized ligand 4'-carboxy-4, 2':6',4''-terpyridine. *Cryst. Eng. Comm.* **2013**, 15, 1460–1467.
- (13) Li, X.; Xie, Z.; Lin, J.; Cao, R. Lanthanide-organic frameworks constructed from multi-functional ligands: syntheses, structures, near-infrared and visible photoluminescence properties. *J. Solid State Chem.* **2009**, 182, 2290–2297.
- (14) Ding, B.; Liu, Y. Y.; Huang, Y. Q.; Shi, W.; Cheng, P.; Liao, D. Z.; Yan, S. P. Structural variations influenced by ligand conformation and counteranions in copper(II) complexes with flexible bis-triazole ligand. *Cryst. Growth Des.* **2009**, 9, 539–601.
- (15) Gai, Y. L.; Jiang, F. L.; Xiong, K. C.; Chen, L.; Yuan, D. Q.; Zhang, L. J.; Zhou, K.; Hong, M. C. Temperature-dependent in situ reduction of 4,4'-aobispyridine via solvothermal reaction. *Cryst. Growth Des.* **2012**, 12, 2079–2088.
- (16) Xie, Z. Q.; Liu, L. L.; Yang, B.; Yang, G. D.; Ye, L.; Li, M.; Ma, Y. G. Polymorphism of 2,5-diphenyl-1,4-distyrylbenzene with two *cis* double bonds: the essential role of aromatic CH/ $\pi$  hydrogen bonds. *Cryst. Growth Des.* **2005**, 5, 1959–1964.
- (17) Khavasi, H. R.; Fard, M. A.  $\pi$ - $\pi$  interactions affect coordination geometries. *Cryst. Growth Des.* **2010**, 10, 1892–1896.
- (18) Husson, J.; Beley, M.; Kirsch, G. A novel pathway for the synthesis of a carboxylic acid-functionalized Ru(II) terpyridine complex. *Tetra. Lett.* **2007**, 44, 1767–1770.

- (19) Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structures*. University of Göttingen, Germany **1997**.
- (20) Faria, D. M.; Yoshida, M. I.; Pinheiro, C. B.; Guedes, K. J.; Krambrock, K.; Diniz, R.; Oliveira, L. F.; Machado, F. C. Preparation, crystal structures and spectroscopic characterization of oxalate copper(II) complexes containing the nitrogen ligands 4,4'-dimethyl-2,2'-bipyridine and di(2-pyridyl)sulfide. *Polyhedron* **2007**, 26, 4525–4532.
- (21) Chen, W.; Wang, J. Y.; Chen, C.; Yue, Q.; Yuan, H. M.; Chen, J. S.; Wang, S. N. Photoluminescent metal-organic polymer constructed from trimetallic clusters and mixed carboxylates. *Inorg. Chem.* **2003**, 42, 944–946.
- (22) Cui, P.; Chen, Z.; Gao, D. L.; Zhao, B.; Shi, W.; Cheng, P. Syntheses, structures, and photoluminescence of a series of three-dimensional Cd(II) frameworks with a flexible ligand 1,5-bis(5-tetrazolo)-3-oxapentane. *Cryst. Growth Des.* **2010**, 10, 4370–4378.
- (23) Ren, H.; Song, T. Y.; Xu, J. N.; Jing, S. B.; Yu, Y.; Zhang, P.; Zhang, L. R. Four novel three-dimensional pillared-layer metal-organic frameworks in the Zn/triazolate/carboxylate system: hydrothermal synthesis, crystal structure, and luminescence properties. *Cryst. Growth Des.* **2009**, 1, 105–112.
- (24) Wang, Z. W.; Ji, C. C.; Li, J.; Guo, Z. J.; Li, Y. Z.; Zheng, H. G. Synthesis, X-ray structures, and fluorescent properties of coordination networks constructed from 2-(2-pyridinyl-benzimidazolyl) acetic anion. *Cryst. Growth Des.* **2009**, 1, 475–482.
- (25) Chu, Q.; Liu, G. X.; Huang, Y. Q.; Wang, X. F.; Sun, W. Y. Syntheses, structures, and optical properties of novel zinc(II) complexes with multicarboxylate and N-donor ligands. *Dalton Trans.* **2007**, 4302–4311.

**Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–O(3)	1.928(7)	Zn(1)–O(5)	2.234(7)	Zn(1)–O(6)	2.127(8)
Zn(1)–N(1)	2.174(9)	Zn(1)–N(3)	2.059(8)	Zn(1)–N(4)	2.203(10)
Angle	(°)	Angle	(°)	Angle	(°)
O(3)–Zn(1)–O(5)	93.4(3)	O(3)–Zn(1)–O(6)	90.0(3)	O(3)–Zn(1)–N(1)	111.1(4)
O(3)–Zn(1)–N(3)	174.0(4)	O(3)–Zn(1)–N(4)	99.0(4)	O(6)–Zn(1)–O(5)	176.0(3)
O(6)–Zn(1)–N(1)	90.5(3)	O(6)–Zn(1)–N(4)	90.3(3)	N(1)–Zn(1)–O(5)	90.2(3)
N(1)–Zn(1)–N(4)	149.9(3)	N(3)–Zn(1)–O(5)	86.8(3)	N(3)–Zn(1)–O(6)	89.6(3)
N(3)–Zn(1)–N(1)	74.9(4)	N(3)–Zn(1)–N(4)	75.0(3)	N(4)–Zn(1)–O(5)	87.1(3)

**Table 2. Selected Bond Lengths (Å) and Bond Angles (°) for 2**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–O(5)	1.969(3)	Zn(1)–O(9)	2.158(3)	Zn(1)–O(10)	2.110(3)
Zn(1)–N(1)	2.284(3)	Zn(1)–N(3)	2.125(3)	Zn(1)–N(4)	2.175(3)
Zn(2)–O(7)	1.938(3)	Zn(2)–O(11)	2.109(3)	Zn(2)–O(12)	2.186(3)
Zn(2)–N(6)	2.242(3)	Zn(2)–N(8)	2.103(3)		
Angle	(°)	Angle	(°)	Angle	(°)
O(5)–Zn(1)–O(9)	86.99(12)	O(5)–Zn(1)–O(10)	96.94(13)	O(5)–Zn(1)–N(1)	87.91(11)
O(5)–Zn(1)–N(3)	159.25(12)	O(5)–Zn(1)–N(4)	123.82(11)	O(9)–Zn(1)–N(1)	94.46(11)
O(9)–Zn(1)–N(4)	89.65(12)	O(10)–Zn(1)–O(9)	175.86(12)	O(10)–Zn(1)–N(1)	87.00(11)
O(10)–Zn(1)–N(3)	89.26(12)	O(10)–Zn(1)–N(4)	87.09(11)	N(3)–Zn(1)–O(9)	87.48(11)
N(3)–Zn(1)–N(1)	72.61(11)	N(3)–Zn(1)–N(4)	76.11(11)	N(4)–Zn(1)–N(1)	148.21(11)
O(7)–Zn(2)–O(11)	94.70(12)	O(7)–Zn(2)–O(12)	85.43(11)	O(7)–Zn(2)–N(6)	96.55(12)
O(7)–Zn(2)–N(8)	165.96(12)	O(7)–Zn(2)–N(9)	114.65(12)	O(11)–Zn(2)–O(12)	176.20(12)
O(11)–Zn(2)–N(6)	85.71(11)	O(11)–Zn(2)–N(9)	89.22(12)	O(12)–Zn(2)–N(6)	90.51(11)
N(8)–Zn(2)–O(11)	94.97(12)	N(8)–Zn(2)–O(12)	84.25(11)	N(8)–Zn(2)–N(6)	74.07(11)
N(8)–Zn(2)–N(9)	75.65(11)	N(9)–Zn(2)–O(12)	94.17(12)	N(9)–Zn(2)–N(6)	148.70(11)

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) for 3

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–O(2)#1	1.9517(16)	Zn(1)–O(7)	2.141(2)	Zn(1)–O(8)	2.215(3)
Zn(1)–N(1)	2.192(2)	Zn(1)–N(3)	2.0879(18)	Zn(1)–N(4)	2.183(2)
Angle	(°)	Angle	(°)	Angle	(°)
O(2)#1–Zn(1)–O(7)	89.49(13)	O(2)#1–Zn(1)–O(8)	92.42(13)	O(2)#1–Zn(1)–N(1)	105.54(10)
O(2)#1–Zn(1)–N(3)	178.46(16)	O(2)#1–Zn(1)–N(4)	103.51(10)	O(7)–Zn(1)–O(8)	175.81(10)
O(7)–Zn(1)–N(1)	92.03(10)	O(7)–Zn(1)–N(4)	87.84(10)	N(1)–Zn(1)–O(8)	91.04(11)
N(3)–Zn(1)–O(7)	91.59(10)	N(3)–Zn(1)–O(8)	86.43(10)	N(3)–Zn(1)–N(4)	75.44(8)
N(4)–Zn(1)–O(8)	88.09(10)	N(4)–Zn(1)–N(1)	150.95(8)		

Table 4. Selected Bond Lengths (Å) and Bond Angles (°) for 4

Bond	Dist.	Bond	Dist.	Bond	Dist.
Zn(1)–O(6)#1	1.993(4)	Zn(1)–O(9)	2.098(4)	Zn(1)–O(10)	2.113(4)
Zn(1)–N(1)	2.210(4)	Zn(1)–N(3)	2.135(4)	Zn(1)–N(4)	2.242(4)
Zn(2)–O(1)#2	2.070(4)	Zn(2)–O(3)	1.945(4)	Zn(2)–O(7)#3	2.358(5)
Zn(2)–O(8)#3	2.089(5)	Zn(2)–O(11)	2.285(6)	Zn(2)–N(5)	2.122(4)
Angle	(°)	Angle	(°)	Angle	(°)
O(6)#1–Zn(1)–O(9)	92.43(16)	O(6)#1–Zn(1)–O(10)	91.51(19)	O(6)#1–Zn(1)–N(1)	124.44(15)
O(6)#1–Zn(1)–N(3)	161.10(15)	O(6)#1–Zn(1)–N(4)	87.28(14)	O(9)–Zn(1)–O(10)	172.51(18)
O(9)–Zn(1)–N(1)	89.61(15)	O(9)–Zn(1)–N(3)	90.20(15)	O(9)–Zn(1)–N(4)	88.47(16)
O(10)–Zn(1)–N(1)	93.39(16)	O(10)–Zn(1)–N(3)	84.03(18)	O(10)–Zn(1)–N(4)	85.36(16)
N(1)–Zn(1)–N(3)	148.27(14)	N(3)–Zn(1)–N(1)	74.27(14)	N(3)–Zn(1)–N(4)	74.07(14)
O(1)#2–Zn(2)–O(7)#3	93.18(17)	O(1)#2–Zn(2)–O(8)#3	93.55(18)	O(1)#2–Zn(2)–O(11)	172.97(18)
O(1)#2–Zn(2)–C(23)#3	95.80(18)	O(3)–Zn(2)–O(1)#2	98.40(17)	O(3)–Zn(2)–O(7)#3	91.47(16)
O(3)–Zn(2)–O(8)#3	148.37(18)	O(3)–Zn(2)–O(11)	86.4(2)	O(3)–Zn(2)–N(5)	114.16(17)
O(3)–Zn(2)–C(23)#3	119.4(2)	O(7)#3–Zn(2)–C(23)#3	28.96(18)	O(8)#3–Zn(2)–O(7)#3	58.57(16)
O(8)#3–Zn(2)–O(11)	79.7(2)	O(8)#3–Zn(2)–N(5)	93.73(17)	O(8)#3–Zn(2)–C(23)#3	29.72(19)
O(11)–Zn(2)–O(7)#3	81.6(2)	O(11)–Zn(2)–C(23)#3	77.3(2)	N(5)–Zn(2)–O(7)#3	151.62(15)
N(5)–Zn(2)–O(11)	87.8(2)	N(5)–Zn(2)–C(23)#3	122.89(18)		

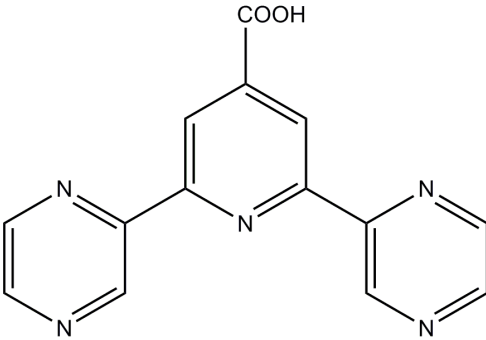


Chart 1. Structure of the Hbpcc ligand

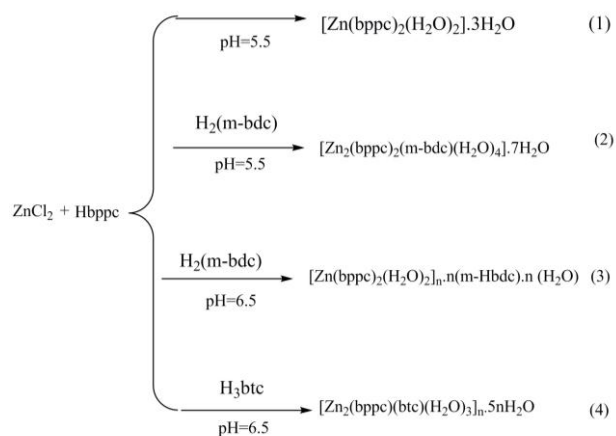
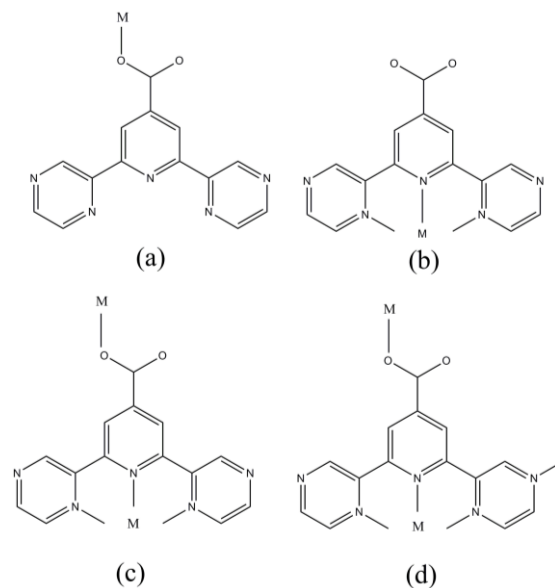
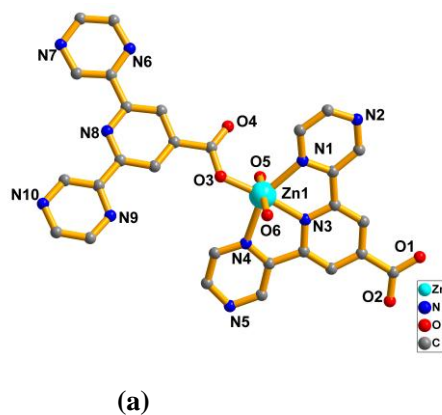
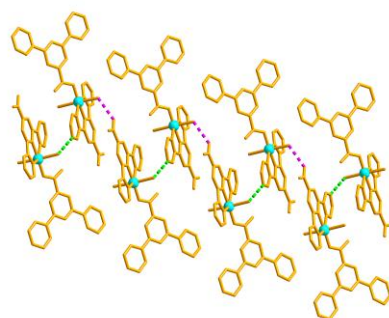
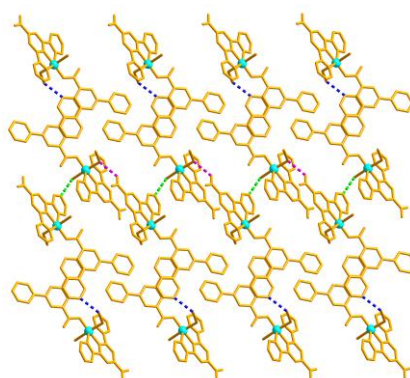


Chart 2. Syntheses of compounds 1~4

Scheme 1. Coordination modes of the (bppc)<sup>-</sup> ligand in 1~4



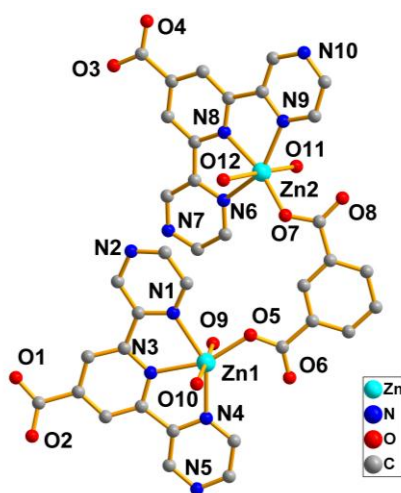
(b)



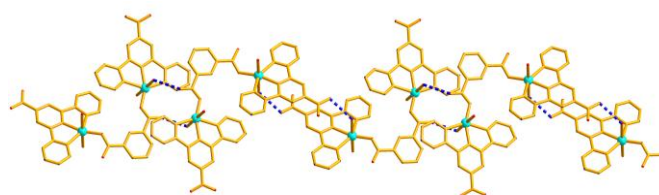
(c)

Fig. 1. (a) Coordination environment of the Zn<sup>II</sup> cations in 1;

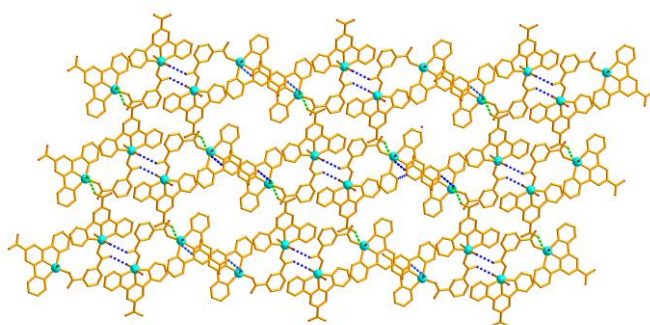
(b) 1D chain structure of 1; (c) Perspective view of the 2D supramolecular framework



(a)



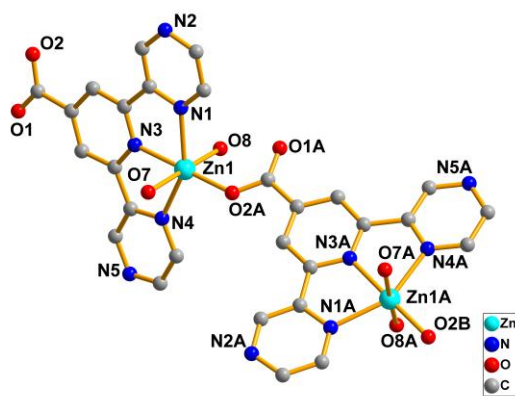
(b)



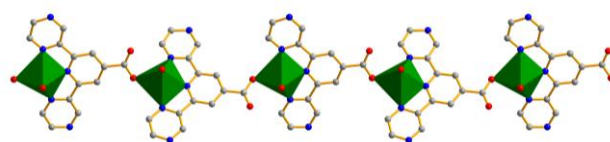
(c)

Fig. 2. (a) Coordination environment of the  $\text{Zn}^{\text{II}}$  cations in **2**; (b) View of the 1D chain formed by hydrogen bonds;

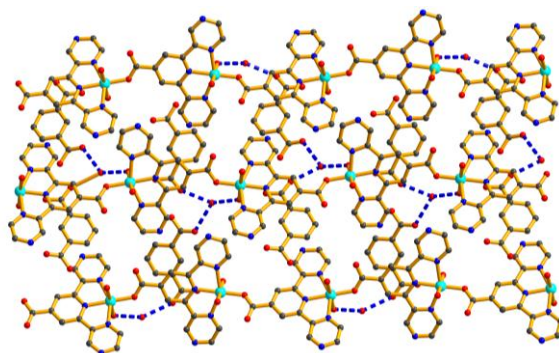
(c) 2D supramolecular framework formed by hydrogen bonds



(a)

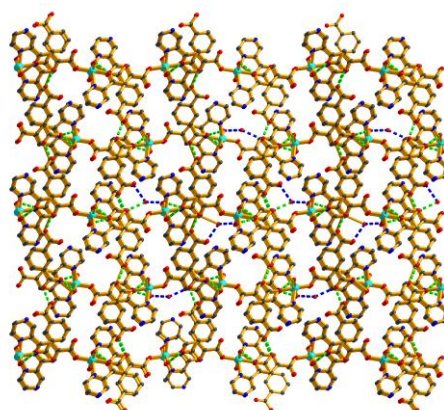


(b)



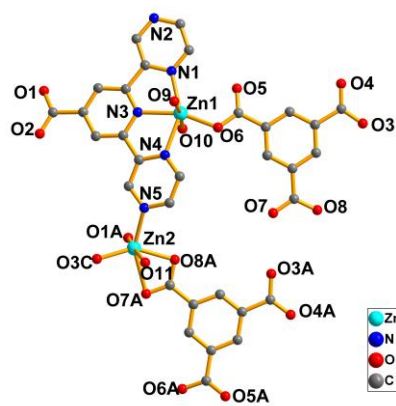
(c)





(d)

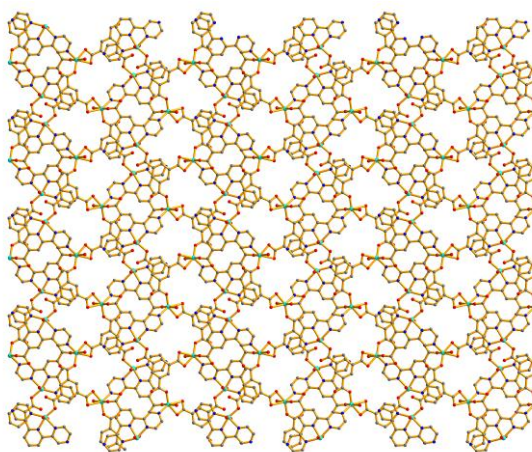
Fig. 3. (a) Coordination environment of the  $\text{Zn}^{\text{II}}$  cation in 3; (b) View of the 1D chain of 3; (c) 2D supramolecular framework of 3; (d) Perspective view of the 3D supramolecular framework of 3



(a)



(b)



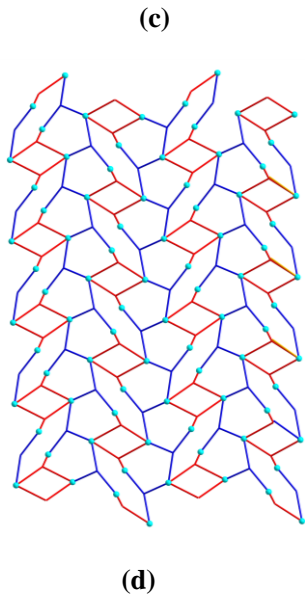


Fig. 4. (a) Coordination environment of the  $\text{Zn}^{\text{II}}$  atom in 4; (b) View of the 1D chain of 4; (c) 2D layer framework of 4; (d) Topological network of 4

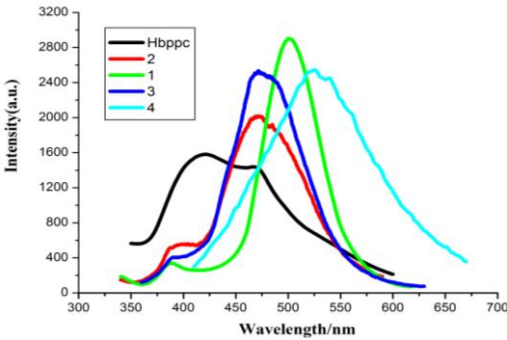
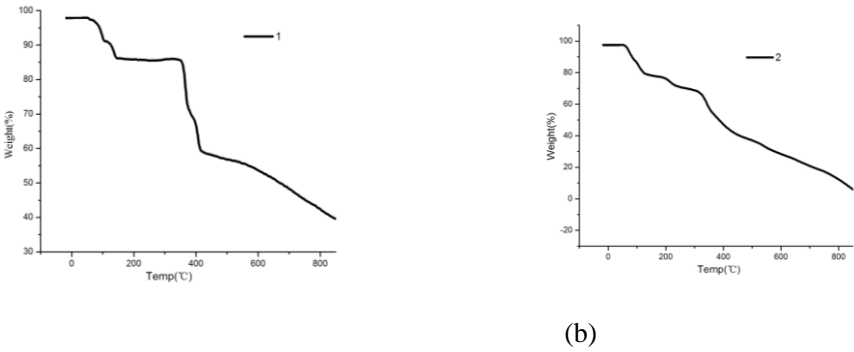


Fig. 5. Solid-state emission spectra of the Hbppc ligand and complexes 1~4 at room temperature





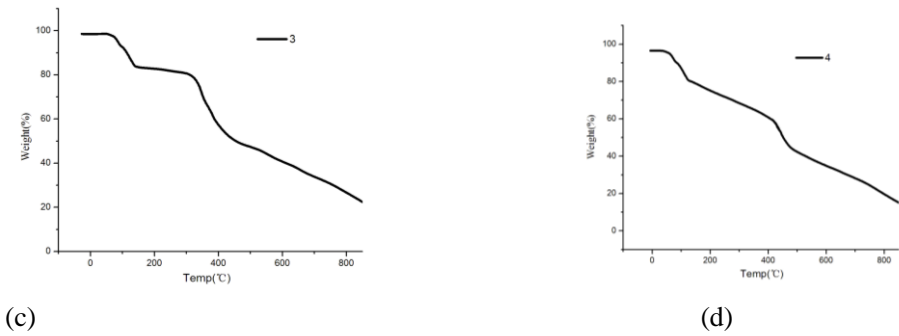


Fig. 6. TGA curves for 1 (a), 2 (b), 3 (c) and 4 (d)

# Effect of pH/Auxiliary Ligand on the Structures of Coordination Compounds

## Based on a Novel Ligand 2,6-Bis(pyrazin-2-yl)pyridine-4-carboxylate

SONG Juan(宋娟) HU Huai-Ming(胡怀明) SHI Juan(史娟)

JI Jian-Wei(季建伟) LU Jiu-Fu(卢久富) GE Hong-Guang(葛红光)

Four new Zn(II) coordination polymers have been synthesized by changing the pH value or auxiliary ligands under hydrothermal conditions. Compounds **1** and **2** show mononuclear structures. Compound **3** features a 1D chain structure. Complex **4** shows a 2D layer structure with a {4.6.8}{4.62.82.10}{62.8}{6} topology.

